

## COATED ARTICLE

### Field of the Invention

This invention relates to articles, in particular brass articles, with a multi-layer decorative and protective coating thereon.

### Background of the Invention

It is currently the practice with various brass articles such as faucets, faucet escutcheons, door knobs, door handles, door escutcheons and the like to first buff and polish the surface of the article to a high gloss and to then apply a protective organic coating, such as one comprised of acrylics, urethanes, epoxies, and the like, onto this polished surface. This system has the drawback that the buffing and polishing operation, particularly if the article is of a complex shape, is labor intensive. Also, the known organic coatings are not always as durable as desired. It would, therefore, be quite advantageous if brass articles, or indeed other articles, such as plastic, ceramic, or metallic, could be provided with a coating which gave the article a decorative appearance such as for example that of highly polished brass and provided wear resistance and corrosion protection. The present invention provides such a coating.

## Summary of the Invention

The present invention is directed to an article such as a plastic, ceramic, or metallic article having a multi-layer coating deposited on at least a portion of its surface. More particularly, it is directed to an article or substrate, particularly a metallic article such as stainless steel, aluminum, brass or zinc, having deposited on its surface superposed layers of certain specific types of materials. The coating is decorative and also provides corrosion resistance and wear resistance. The coating, in one embodiment, provides the appearance of highly polished brass, i.e. has a brass color tone. Thus, an article surface having the coating thereon simulates a highly polished brass surface.

The article first has deposited on its surface one or more plated layers. On top of the plated layers is then deposited, by vapor deposition, one or more vapor deposited layers.

A first layer deposited directly on the surface of the substrate is comprised of nickel. The first layer may be monolithic or it may consist of two different nickel layers such as, for example, a semi-bright nickel layer deposited directly on the surface of the substrate and a bright nickel layer superimposed over the semi-bright nickel layer. Disposed over the nickel layer is a layer comprised of a non-precious refractory metal or metal alloy such as zirconium, titanium, hafnium, tantalum, or zirconium-titanium alloy, preferably zirconium, titanium, or zirconium-

titanium alloy. Over the layer comprised of refractory metal or refractory metal alloy is a layer comprised of non-precious refractory metal compound or metal alloy compound.

The nickel layer is applied by plating, such as for example electroplating. The non-precious refractory metal or non-precious refractory metal alloy layer and the non-precious refractory metal compound or non-precious refractory metal alloy compound layer are applied by vapor deposition such as cathodic arc evaporation or sputtering.

#### Brief Description of the Drawings

FIG. 1 is a cross-sectional view, not to scale, of a portion of the substrate having the multi-layer coating deposited by electroplating and vapor deposition on its surface; and

FIG. 2 is a view similar to Fig. 1 except that the vapor deposited coating is applied directly onto the surface of the article without any intervening plated layers.

#### Description of the Preferred Embodiment

The article or substrate 12 can be comprised of any material such as plastic, ceramic, metal or metallic alloy. Preferably, it is a platable metal or metallic alloy such as copper, steel, brass, zinc, aluminum, nickel alloys, and the like. In preferred embodiments the substrate is brass or zinc.

In one embodiment of the instant invention, as illustrated in Fig. 1, a first series of layers is applied onto the surface of the

article by plating such as electroplating or electroless plating. A second series of layers is applied onto the surface of the plated layer or layers by vapor deposition such as physical vapor deposition or chemical vapor deposition. In this embodiment a nickel layer 13 may be deposited on the surface of the substrate 12 by conventional and well-known plating processes such as electroplating processes. These processes include using a conventional electroplating bath such as, for example, a Watts bath as the plating solution. Typically such baths contain nickel sulfate, nickel chloride, and boric acid dissolved in water. All chloride, sulfamate and fluoroborate plating solutions can also be used. These baths can optionally include a number of well known and conventionally used compounds such as leveling agents, brighteners, and the like. To produce specularly bright nickel layer at least one brightener from class I and at least one brightener from class II is added to the plating solution. Class I brighteners are organic compounds which contain sulfur. Class II brighteners are organic compounds which do not contain sulfur. Class II brighteners can also cause leveling and, when added to the plating bath without the sulfur-containing class I brighteners, result in semi-bright nickel deposits. These class I brighteners include alkyl naphthalene and benzene sulfonic acids, the benzene and naphthalene di- and trisulfonic acids, benzene and naphthalene sulfonamides, and sulfonamides such as saccharin, vinyl and allyl

sulfonamides and sulfonic acids. The class II brighteners generally are unsaturated organic materials such as, for example, acetylenic or ethylenic alcohols, ethoxylated and propoxylated acetylenic alcohols, coumarins, and aldehydes. These Class I and Class II brighteners are well known to those skilled in the art and are readily commercially available. They are described, inter alia, in U.S. Patent No. 4,421,611 incorporated herein by reference.

The nickel layer can be comprised of a monolithic layer such as semi-bright nickel or bright nickel, or it can be a duplex layer containing two different nickel layers, for example, a layer comprised of semi-bright nickel and a layer comprised of bright nickel. The thickness of the nickel layer is generally in the range of from about 100 millionths (0.000100) of an inch, preferably about 150 millionths (0.000150) of an inch to about 3,500 millionths (0.0035) of an inch.

As is well known in the art before the nickel layer is deposited on the substrate the substrate is subjected to acid activation by being placed in a conventional and well known acid bath.

In one embodiment as illustrated in Fig. 1, the nickel layer 13 is actually comprised of two different nickel layers 14 and 16. Layer 14 is comprised of semi-bright nickel while layer 16 is comprised of bright nickel. This duplex nickel deposit provides

improved corrosion protection to the underlying substrate. The semi-bright, sulfur-free plate 14 is deposited by conventional electroplating processes directly on the surface of substrate 12. The substrate 12 containing the semi-bright nickel layer 14 is then placed in a bright nickel plating bath and the bright nickel layer 16 is deposited on the semi-bright nickel layer 14.

The thickness of the semi-bright nickel layer and the bright nickel layer is a thickness effective to provide improved corrosion protection. Generally, the thickness of the semi-bright nickel layer is at least about 50 millionths (0.00005) of an inch, preferably at least about 100 millionths (0.0001) of an inch, and more preferably at least about 150 millionths (0.00015) of an inch. The upper thickness limit is generally not critical and is governed by secondary considerations such as cost. Generally, however, a thickness of about 1,500 millionths (0.0015) of an inch, preferably about 1,000 millionths (0.001) of an inch, and more preferably about 750 millionths (0.00075) of an inch should not be exceeded. The bright nickel layer 16 generally has a thickness of at least about 50 millionths (0.00005) of an inch, preferably at least about 125 millionths (0.000125) of an inch, and more preferably at least about 250 millionths (0.00025) of an inch. The upper thickness range of the bright nickel layer is not critical and is generally controlled by considerations such as cost. Generally, however, a thickness of about 2,500 millionths (0.0025) of an inch, preferably

about 2,000 millionths (0.002) of an inch, and more preferably about 1,500 millionths (0.0015) of an inch should not be exceeded. The bright nickel layer 16 also functions as a leveling layer which tends to cover or fill in imperfections in the substrate.

Disposed over nickel layer 13 is a layer 22 comprised of a non-precious refractory metal or metal alloy such as hafnium, tantalum, zirconium, titanium or zirconium-titanium alloy, preferably zirconium, titanium or zirconium-titanium alloy, and more preferably zirconium.

Layer 22 is deposited on the nickel layer by conventional and well known techniques including vapor deposition processes including chemical vapor deposition and physical vapor deposition such as cathodic arc evaporation (CAE) or sputtering, and the like. Sputtering techniques and equipment are disclosed, inter alia, in J. Vossen and W. Kern "Thin Film Processes II", Academic Press, 1991; R. Boxman et al, "Handbook of Vacuum Arc Science and Technology", Noyes Pub., 1995; and U.S. patent Nos. 4,162,954, and 4,591,418, all of which are incorporated herein by reference.

Briefly, in the sputtering deposition process a refractory metal (such as titanium or zirconium) target, which is the cathode, and the substrate are placed in a vacuum chamber. The air in the chamber is evacuated to produce vacuum conditions in the chamber. An inert gas, such as Argon, is introduced into the chamber. The gas particles are ionized and are accelerated to the target to

dislodge titanium or zirconium atoms. The dislodged target material is then typically deposited as a coating film on the substrate.

In cathodic arc evaporation, an electric arc of typically several hundred amperes is struck on the surface of a metal cathode such as zirconium or titanium. The arc vaporizes the cathode material, which then condenses on the substrates forming a coating.

Layer 22 is a strike layer and has a thickness which is generally at least effective to improve the adhesion of layer 32 to layer 21. Generally this thickness is at least about 0.25 millionths (0.00000025) of an inch, preferably at least about 0.5 millionths (0.0000005) of an inch, and more preferably at least about one millionth (0.000001) of an inch. The upper thickness range is not critical and is generally dependent upon considerations such as cost. Generally, however, layer 22 should not be thicker than about 50 millionths (0.00005) of an inch, preferably about 15 millionths (0.000015) of an inch, and more preferably about 10 millionths (0.000010) of an inch.

In a preferred embodiment of the present invention layer 22 is comprised of titanium, zirconium or zirconium-titanium alloy, preferably zirconium or zirconium-titanium alloy, and is deposited by sputtering or cathodic arc evaporation.

Deposited over the refractory metal or refractory metal alloy layer 22 is a layer 32 comprised of a non-precious refractory metal



compound or non-precious refractory metal alloy compound, such as an oxide, nitride, carbide or carbonitride, preferably a nitride, carbide or carbonitride, and more preferably a nitride.

Layer 32 is comprised of a hafnium compound, a tantalum compound, a titanium compound, a zirconium-titanium alloy compound, or a zirconium compound, preferably a titanium compound, a zirconium-titanium alloy compound, or a zirconium compound, and more preferably a zirconium compound or a zirconium-titanium alloy compound. The compounds are selected from the oxides, carbides, carbonitrides and nitrides, with the carbides, carbonitrides and nitrides being preferred. Thus, the titanium compound is preferably selected from titanium nitride, titanium carbide, and titanium carbonitride, with titanium nitride being more preferred. The zirconium compound is preferably selected from zirconium nitride, zirconium carbonitride, and zirconium carbide, with zirconium nitride being more preferred.

Layer 32 provides wear and abrasion resistance and the desired color or appearance, such as for example, polished brass. Layer 32 is deposited on layer 22 by any of the well known and conventional vapor deposition techniques such as, for example, reactive sputtering and reactive cathodic arc evaporation.

Reactive cathodic arc evaporation and reactive sputtering are generally similar to ordinary sputtering and cathodic arc evaporation except that a reactive gas is introduced into the

chamber which reacts with the dislodged target material. Thus, in the case where zirconium nitride is the layer 32, the cathode is comprised of zirconium and nitrogen is the reactive gas introduced into the chamber. By controlling the amount of nitrogen available to react with the zirconium, the color of the zirconium nitride can be adjusted to be similar to that of brass of various hues.

Layer 32 has a thickness at least effective to provide abrasion resistance and the desired color or appearance. Generally, this thickness is at least 0.1 millionths (0.000001) of an inch, preferably at least 1 millionth (0.000001) of an inch, and more preferably at least 2 millionths (0.000002) of an inch. The upper thickness range is generally not critical and is dependent upon secondary considerations such as cost. Generally a thickness of about 30 millionths (0.00003) of an inch, preferably about 25 millionths (0.000025) of an inch, and more preferably about 20 millionths (0.000020) of an inch should not be exceeded.

In one embodiment zirconium nitride is a preferred coating material as it most closely provides the appearance of polished brass.

In the embodiment illustrated in Fig. 2 the vapor deposited coating layers 22 and 32 are applied directly onto the surface of the substrate 12 without the presence of any intervening nickel layers. Reference numerals 22 and 32 represent the same layers as described supra with respect to Fig. 1.

In order that the invention may be more readily understood the following example is provided. The example is illustrative and does not limit the invention thereto.

#### EXAMPLE 1

Brass faucets are placed in a conventional soak cleaner bath containing the standard and well known soaps, detergents, defloculants and the like which is maintained at a pH of 8.9 - 9.2 and a temperature of 180 - 200°F for about 10 minutes. The brass faucets are then placed in a conventional ultrasonic alkaline cleaner bath. The ultrasonic cleaner bath has a pH of 8.9 - 9.2, is maintained at a temperature of about 160 - 180°F, and contains the conventional and well known soaps, detergents, defloculants and the like. After the ultrasonic cleaning the faucets are rinsed and placed in a conventional alkaline electro cleaner bath. The electro cleaner bath is maintained at a temperature of about 140 - 180°F, a pH of about 10.5 - 11.5, and contains standard and conventional detergents. The faucets are then rinsed twice and placed in a conventional acid activator bath. The acid activator bath has a pH of about 2.0 - 3.0, is at an ambient temperature, and contains a sodium fluoride based acid salt. The faucets are then rinsed twice and placed in a bright nickel plating bath for about 12 minutes. The bright nickel bath is generally a conventional bath which is maintained at a temperature of about 130 - 150°F, a pH of about 4.0, contains  $\text{NiSO}_4$ ,  $\text{NiCl}_2$ , boric acid, and brighteners.

A bright nickel layer of an average thickness of about 400 millionths (0.0004) of an inch is deposited on the faucet surface. The faucets are thoroughly rinsed in deionized water and then dried. The nickel plated faucets are placed in a cathodic arc evaporation plating vessel. The vessel is generally a cylindrical enclosure containing a vacuum chamber which is adapted to be evacuated by means of pumps. A source of argon gas is connected to the chamber by an adjustable valve for varying the rate of flow of argon into the chamber. In addition, a source of nitrogen gas is connected to the chamber by an adjustable valve for varying the rate of flow of nitrogen into the chamber.

A cylindrical cathode is mounted in the center of the chamber and connected to negative outputs of a variable D.C. power supply. The positive side of the power supply is connected to the chamber wall. The cathode material comprises zirconium.

The plated faucets are mounted on spindles, 16 of which are mounted on a ring around the outside of the cathode. The entire ring rotates around the cathode while each spindle also rotates around its own axis, resulting in a so-called planetary motion which provides uniform exposure to the cathode for the multiple faucets mounted around each spindle. The ring typically rotates at several rpm, while each spindle makes several revolutions per ring revolution. The spindles are electrically isolated from the

chamber and provided with rotatable contacts so that a bias voltage may be applied to the substrates during coating.

The vacuum chamber is evacuated to a pressure of about  $5 \times 10^{-3}$  millibar and heated to about  $150^{\circ}\text{C}$ .

The electroplated faucets are then subjected to a high-bias arc plasma cleaning in which a (negative) bias voltage of about 500 volts is applied to the electroplated faucets while an arc of approximately 500 amperes is struck and sustained on the cathode. The duration of the cleaning is approximately five minutes.

Argon gas is introduced at a rate sufficient to maintain a pressure of about  $3 \times 10^{-2}$  millibars. A layer of zirconium having an average thickness of about 4 millionths (0.000004) of an inch is deposited on the chrome plated faucets during a three minute period. The cathodic arc deposition process comprises applying D.C. power to the cathode to achieve a current flow of about 500 amps, introducing argon gas into the vessel to maintain the pressure in the vessel at about  $1 \times 10^{-2}$  millibar, and rotating the faucets in a planetary fashion described above.

After the zirconium layer is deposited the zirconium nitride layer is applied onto the zirconium layer. A flow of nitrogen is introduced into the vacuum chamber while the arc discharge continues at approximately 500 amperes. The nitrogen flow rate is sufficient to fully react the zirconium atoms arriving at the substrate to form zirconium nitride.

The nitrogen flow rate is left at its maximum for a time of five to ten minutes to form a zirconium nitride layer on top of the zirconium layer. The arc is extinguished at the end of this last deposition period, the vacuum chamber is vented and the coated substrates removed.

While certain embodiments of the invention have been described for purposes of illustration, it is to be understood that there may be various embodiments and modifications within the general scope of the invention.